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DESCRIPTION

REINFORCING CORD FOR RUBBER REINFORCEMENT AND RUBBER PRODUCT INCLUDING THE SAME

Technical Field

The present invention relates to a reinforcing cord for rubber reinforcement and a rubber product reinforced with a reinforcing cord for rubber reinforcement.

Background Art

Reinforcing fibers such as glass fibers and aramid fibers have been used as reinforcing materials for rubber products such as rubber belts, tires, etc. However, these rubber products are subjected to bending stress repeatedly and thereby the performance thereof tends to deteriorate due to bending fatigue. This tends to cause separation between reinforcing fibers and a rubber matrix, or deterioration in strength due to fraying of the reinforcing fibers. On the other hand, a toothed rubber belt that is used for a camshaft drive of an internal-combustion engine of an automobile requires high dimensional stability in order to maintain appropriate timing. Furthermore, rubber belts that are used for not only the camshaft drive but also an auxiliary drive of, for instance, an injection pump, and power transmission in an industrial machine are required to have high elasticity and high strength to bear a high load.

Under such circumstances, new materials have been studied as reinforcing fibers for rubber belts. Recently, for instance, polyarylate fibers also have been proposed (see JP 2003-294086 A).

As described above, the reinforcing cord for rubber reinforcement is required to have high strength, high elasticity, flexibility in bending, wear resistance, etc. In the conventional cords, however, it was difficult to achieve a balance between the strength and the flexibility. For example, when polyarylate fibers are used as reinforcing fibers, a cord with high strength and high elasticity can be obtained. In this cord, however, bending fatigue tends to occur and thereby the strength thereof tends to deteriorate, which has been a problem.

Disclosure of Invention

With such a situation in mind, the present invention is intended to provide a reinforcing cord for rubber reinforcement having high strength, elasticity, and bending fatigue resistance, and a rubber product including the same.

In order to achieve the above-mentioned object, the present inventors made studies. As a result, they found out that an effect that was more prominent than that they had expected was acquired by combining polyarylate fibers and glass fibers in a specific arrangement. Based on this new knowledge, the present invention described below was achieved.

The reinforcing cord for rubber reinforcement of the present invention is a reinforcing cord for rubber reinforcement that includes reinforcing fibers. The reinforcing fibers include polyarylate fibers and a plurality of outer strands that are arranged around the polyarylate fibers. The outer strands include fibers other than polyarylate fibers. In this specification, the term "strand" implies those obtained by bundling a plurality of filament fibers without twisting them, those obtained by bundling and twisting a plurality of filament fibers, those obtained by bundling a plurality of strands without twisting them, and those obtained by bundling and twisting a plurality of strands.

A rubber product of the present invention includes the reinforcing cord for rubber reinforcement of the present invention described above.

According to the present invention, a reinforcing cord for rubber reinforcement can be obtained that has high strength, elasticity, and bending fatigue resistance and is excellent in dimensional stability. Particularly, when a polyarylate fiber strand and glass fiber strands are combined in a specific arrangement, a reinforcing cord for rubber reinforcement can be obtained that has considerably high bending fatigue resistance. The rubber product of the present invention includes the above-mentioned cord and therefore has high strength, elasticity, and bending fatigue resistance and is excellent in dimensional stability.

Brief Description of Drawings

FIG. 1 is a cross-sectional view that schematically shows an example of the reinforcing cord for rubber reinforcement of the present invention.

FIG. 2 is a schematic view showing a bending test method employed in Example.

Description of the Invention

Embodiments of the present invention are described below.

Embodiment 1

In Embodiment 1, the description is directed to a reinforcing cord for rubber reinforcement of the present invention. A reinforcing cord for rubber reinforcement of the present invention includes reinforcing fibers. The reinforcing fibers include polyarylate fibers and a plurality of strands (outer strands) that are arranged around the polyarylate fibers. The outer strands include fibers (hereinafter may be referred to as "second fibers" in some cases) other than polyarylate fibers.

The polyarylate fibers are wholly aromatic polyester fibers. They can be obtained through polycondensation of dihydric phenol (for example, bisphenol A) and aromatic dicarboxylic acid (for example, phthalic acid or isophthalic acid).

Preferably, the second fibers are fibers whose flexibility in bending is higher than that of the polyarylate fibers. Examples of the second fibers to be used herein include glass fibers, polyparaphenylene benzobisoxazole fibers, carbon fibers, aramid fibers such as polyparaphenylene terephthalamide fibers, and mixed fibers thereof. Preferably, the outer strands are formed of at least one type of fibers selected from glass fibers, polyparaphenylene benzobisoxazole fibers, carbon fibers, and aramid fibers (preferably polyparaphenylene terephthalamide fibers, this also applies to the following). It is particularly preferable that the outer strands be formed of glass fibers or aramid fibers.

When the ratio of the polyarylate fibers in the reinforcing fibers becomes higher, the elastic modulus and dimensional stability improve, but the dynamic flexibility deteriorates. On the other hand, when the ratio becomes lower, the elastic modulus and dimensional stability deteriorate. Accordingly, it is preferable that the ratio of the polyarylate fibers to the whole reinforcing fibers be in the range of 20 vol.% to 80 vol.% (preferably 30 vol.% to 70 vol.%).

In the reinforcing cord for rubber reinforcement of the present invention, it is preferable that the above-mentioned polyarylate fibers form a strand of polyarylate fibers. In this case, the reinforcing cord for rubber reinforcement includes a core strand of polyarylate fibers and a plurality of outer strands that are arranged around the core strand. Preferably, the core

strand is formed substantially of polyarylate fibers. Typically, the core strand is formed of polyarylate fibers alone.

In the cord of the present invention, it is particularly preferable that polyarylate fibers (preferably a strand of polyarylate fibers) with a high elastic modulus be arranged near the center of the cord, while outer strands that are excellent in flexibility and wear resistance be arranged around the polyarylate fibers. The characteristics of the polyarylate fibers arranged near the center of the cord allow the cord to have high strength and a high elastic modulus as well as excellent dimensional stability. The outer strands may be formed of fibers (for example, glass fibers) whose elastic modulus is lower than that of the polyarylate fibers. When such outer strands are used, a reinforcing cord for rubber reinforcement can be obtained that has high strength, elasticity, and bending fatigue resistance.

The diameter, elastic modulus, etc. of the polyarylate fibers are not particularly limited. They are selected according to the characteristics that are required for the reinforcing cord. For instance, polyarylate fibers may be used that have a density of approximately 1.2 g/cm^3 to 2.0 g/cm^3. Furthermore, polyarylate fibers with an elastic modulus (Young's modulus) of approximately 70 GPa to 120 GPa also may be used.

The polyarylate fibers may be those that have not been twisted nor been treated. They, however, may be those to which an adhesive has been applied or those that have been twisted in order to improve the adhesiveness or to prevent them from fraying. The adhesive is not particularly limited but can be an epoxy compound, an isocyanate compound, a treatment solution (hereinafter may be referred to as a "RFL treatment solution") that contains rubber latex and the initial condensate of resorcin and formaldehyde as its main components, etc. The number of twists of the polyarylate fibers (the core strand) is not particularly limited. It generally is preferably 8.0 times/25 mm or less, for example, in the range of 0.5 to 5.0 times/25 mm. When the polyarylate fibers are to be twisted, it is preferable that they be twisted after the treatment solution is applied thereto. When the treatment solution is applied to them after they are twisted, the strand of the polyarylate fibers may tend to fray in some cases.

The thickness of the outer strands as well as the number and diameter of the fibers of each outer strand are not particularly limited. They are selected according to the characteristics that are required for the reinforcing cord. Furthermore, the number of the outer strands that are

arranged around the polyarylate fibers is usually approximately 3 to 20.

Like the outer strands, the strands that are arranged near the periphery of the cord are required to ease the compressive stress and tensile stress that are caused when the cord is bent. Preferable strands that satisfy such requirements are glass fiber strands and aramid fiber strands. When the glass fiber strands that contain glass fibers as their main fibers (at least 50 vol.%, preferably at least 60 vol.%, for example, 100 vol.%) are arranged around a core strand formed of polyarylate fibers, a reinforcing cord for rubber reinforcement can be obtained that has particularly high strength, elasticity, and bending fatigue resistance. Moreover, when glass fiber strands are used as the outer strands, a reinforcing cord can be obtained that adheres strongly to the rubber in which it is to be embedded. For the glass fibers, E-glass filaments or high-strength glass filaments are used preferably, for example. Strands with a thickness of approximately 20 to 480 tex, each of which is obtained by bundling and primarily twisting approximately 200 to 2400 glass filaments with a diameter of 7 to 9 μm, are used preferably as the glass fiber strands.

The outer strands may be primarily twisted. When the outer strands that are arranged near the periphery of the cord are twisted (primarily twisted), the bending fatigue resistance of the cord can be improved. The number of twists is not particularly limited. Preferably, it is approximately 0.25 to 5.0 times/25 mm.

Furthermore, the plurality of outer strands may be wound spirally (i.e. may be finally twisted) with the polyarylate fibers used as a core. The number of twists of the final twist can be approximately 0.5 to 10 times/25 mm, for example. In the case where the outer strands are primarily twisted and are finally twisted, the direction of the final twist may be identical to the direction of the primary twist or may be different from it. When the final twist and the primary twist are carried out in the same direction, a cord with particularly high flexibility in bending can be obtained. In addition, high dimensional stability is obtained when the final twist and the primary twist are carried out in different directions from each other.

With respect to the reinforcing cord for rubber reinforcement of the present invention, it is preferable that the surface thereof be coated with a coating film containing rubber. Usually, the coating film is selected according to the rubber (matrix rubber) in which the cord is to be embedded. The method of forming the coating film is not particularly limited and a

well-known method therefore can be used. For instance, after a treatment solution containing rubber is applied to the cord, it is heat-treated or is dried and thereby a coating film can be formed. The treatment solution to be used herein can be the RFL treatment solution, for example. Examples of the rubber latex to be used for the RFL treatment solution include an acrylic-rubber-based latex, a urethane-based latex, a chlorosulfonated-polyethylene-based latex, denatured latexes thereof, mixtures thereof, etc.

The peripheries of the fiber strands and the periphery of the cord may be coated with coating films whose materials are different from each other. For example, in order to improve the adhesiveness between the matrix rubber of a rubber product and the cord of the present invention, the periphery of the cord may be subjected to an overcoating treatment. The overcoating treatment can be carried out using a treatment solution containing a crosslinker and rubber such as hydrogenated nitrile rubber, chlorosulfonated polyethylene rubber (CSM), chloroprene rubber, crude rubber, or urethane rubber, for example. Usually, the rubber to be used for the overcoating treatment is selected according to the type of the matrix rubber. The amount of the overcoat is not particularly limited. For example, it may be in the range of 2.0 to 10.0 parts by mass with respect to 100 parts by mass of the cord obtained before the overcoating treatment.

FIG. 1 shows a cross-sectional view of a preferable example of the reinforcing cord for rubber reinforcement of the present invention. A cord 10 shown in FIG. 1 includes: polyarylate fibers (a core strand) 11 arranged in the center of the cord 10; a plurality of outer strands 12 arranged around the polyarylate fibers 11; and a coating film 13 (hatching thereof is omitted) with which both the polyarylate fibers 11 and the outer strands 12 are coated. The plurality of outer strands 12 are wound spirally around the polyarylate fibers 11. The coating film 13 contains rubber.

A method of producing the cord 10 is described below. The outer strands 12 each can be formed by bundling fibers. A coating film may be formed around the polyarylate fibers (the core strand) and/or the outer strands by carrying out a treatment, for example, a RFL treatment as required. Furthermore, the polyarylate fibers (the core strand) and/or the outer strands may be twisted as required. Moreover, a plurality of strands may be twisted to form one strand as required.

Next, the outer strands 12 are arranged around the polyarylate fibers

11. This process can be carried out using a guide that has a center guide hole and a plurality of peripheral guide holes arranged on a circle that shares its center with the center guide hole, for example. One polyarylate fiber 11 or a plurality of polyarylate fibers 11 that have not been twisted or have been primarily twisted are allowed to pass through the center guide hole, while the outer strands 12 are allowed to pass through the plurality of peripheral guide holes. Furthermore, when the guide is not used, a tension that is at least 1.2 times the tension that is applied to the peripheral fibers may be applied to the center fibers. When a higher tension than the tension that is applied to the peripheral fibers is applied to the center fibers, the arrangement of the center fibers is facilitated and thereby the same effect as that obtained when the guide is used is obtained. The outer strands 12 are primarily twisted as required. The devices for doubling and twisting the strands are not particularly limited. For example, a ring twisting frame, a flyer twisting frame, or a twisting machine can be used.

Finally, the coating film 13 is formed so as to coat the whole of the polyarylate fibers 11 and the outer strands 12. Thus, the cord 10 is produced.

The cord of the present invention may be used independently (as a rope structure). Furthermore, the cord of the present invention may be used in a bamboo-blind-like structure, i.e., a structure in which a plurality of cords are arranged in the form of a sheet and are attached to each other loosely.

Embodiment 2

In Embodiment 2, the description is directed to a rubber product of the present invention. The rubber product of the present invention includes at least one reinforcing cord for rubber reinforcement described in Embodiment 1. This reinforcing cord for rubber reinforcement may be a rope structure. Furthermore, a plurality of reinforcing cords for rubber reinforcement may be arranged and embedded in the shape of a sheet.

The rubber product of the present invention is not particularly limited as long as it is a rubber product reinforced effectively with the reinforcing cord for rubber reinforcement. Typical examples of the rubber product of the present invention include rubber belts such as a toothed belt and a move belt, and a rubber crawler.

In the rubber product of the present invention, the ratio of the reinforcing cord for rubber reinforcement to the rubber product is approximately 10 to 70 wt.%, for example.

EXAMPLE

Hereinafter, the present invention is described further in detail using examples. In the examples, reinforcing cords for rubber reinforcement of the present invention and comparative examples were produced, and then the characteristics thereof were evaluated.

Sample 1

A reinforcing cord for rubber reinforcement of the present invention was produced by the following method. First, a resorcinol-formaldehyde condensate (with a solid content of 8 wt.%), vinyl pyridine-styrene-butadiene latex (with a solid content of 40 wt.%), and CSM (with a solid content of 40 wt.%) were mixed together in such a manner as to have a solid content mass ratio of 2 : 13 : 6. Thus, a RFL treatment solution was prepared. This RFL treatment solution was applied to a strand (with a diameter of approximately 0.8 mm; a non-twisted product) formed of polyarylate fibers (with an elastic modulus of 106 GPa and a density of approximately 1.41 g/cm^3; Vectran (Trade Name); manufactured by KURARAY CO., LTD.). Thereafter, this was heat-treated (at 180°C for 120 seconds) to be dried. Thus, a core strand (the amount of RFL that had adhered thereto: 20 wt.%) that had been subjected to the RFL treatment was obtained.

On the other hand, a bundle of 600 glass fibers (with a diameter of 9 μm, an elastic modulus of 70 GPa, and a density of approximately 2.5 g/cm^3; E Glass; manufactured by Nippon Sheet Glass Co., Ltd.) that had been aligned with one another was impregnated with a RFL treatment solution. Thereafter, this was heat-treated (at 180°C for 120 seconds) to be dried. Then, it was primarily twisted in the S direction at a rate of 2.0 times/25 mm. Thus, a glass fiber strand (the amount of RFL that had adhered thereto: 20 wt.%) of approximately 100 tex was obtained.

Next, nine glass fiber strands were arranged around the core strand that had been subjected to the RFL treatment, in such a manner as to be arranged as shown in FIG. 1. This was finally twisted in the Z direction at a rate of 2.0 times/25 mm. Thus, a cord 1A was obtained. The diameter of the cord 1A was approximately 1.20 mm. The ratio of the sectional area of the polyarylate fibers to that of the whole fibers was 45%.

Next, an overcoat treatment solution whose components are indicated in Table 1 below was applied to the cord 1A, which then was dried. Thus, a cord 1B was obtained. The amount of the solid content of the overcoat treatment solution that had adhered to the cord 1B was 5 wt.%. The linear

density (the weight (g) per length of 1000 m) of the cord 1B was 1580 tex (g/1000 m). With respect to the cord 1B thus obtained, the tensile strength and the elongation (%) at rupture were measured. The tensile strength (initial) per cord 1B was 1250 N/cord, while the elongation at rupture was 3.2%.

Table 1

Components	Ratio (Parts by Mass)
CSM (Trade Name: TS-340, manufactured by Tosoh Corporation; chlorine content: 43 wt.%, sulfur content: 1.1 wt.%)	5.25
P-dinitrosobenzene	2.25
Carbon Black	3.0
Mixed Solvent of Xylene and Trichlorethylene (Mass Ratio between Xylene and Trichlorethylene = 1.5 : 1.0)	85.0

In addition, two rubber sheets (with a width of 10 mm, a length of 300 mm, and a thickness of 1 mm) were prepared that contained the components indicated in Table 2 below.

Table 2

Components	Ratio (Parts by Mass)
Hydrogenated Acrylonitrile-Butadiene Rubber (Zetpol 2020, manufactured by ZEON CORPORATION)	100
Zinc Oxide, Grade 1	5
Stearic Acid	1.0
HAF Carbon	60
Trioctyl Trimellitate	10
4,4-(α,α-dimethylbenzyl)diphenylamine	1.5
2-mercaptobenzimidazole Zinc Salt	1.5
Sulfur	0.5
Tetramethylthiuramsulfide	1.5
Cyclohexyl-Benzothiazylsulfenamide	1.0

One cord 1B with a length of 300 mm was placed on one rubber sheet and the other rubber sheet was placed thereon. This was pressed from the upper and lower sides thereof at 150°C for 20 minutes to be cured. Thus a belt-shaped specimen was produced.

Next, with respect to this specimen, a bending test was carried out with a bending tester 20 shown in FIG. 2. The bending tester 20 was

provided with one flat pulley 21 having a diameter of 25 mm, a motor (not shown in FIG. 2), and four guide pulleys 22. First, the specimen 23 produced as above was placed on the five pulleys. Then a weight was attached to one end 23a of the specimen 23 to apply an initial tension of 9.8 N to the specimen 23. In this state, the other end 23b of the specimen 23 was reciprocated 10000 times for a distance of 10 cm in the directions indicated with a double-headed arrow in FIG. 2. Thus the specimen 23 was bended repeatedly around the flat pulley 21. The bending test was carried out at room temperature. After the specimen 23 was subjected to the bending test as described above, the tensile strength of the specimen was measured. Then the tensile-strength retention rate (%) of the specimen after the bending test was determined, with the tensile strength of the specimen before the bending test being taken as 100%. The higher the tensile-strength retention rate, the better the bending fatigue resistance. The specimen of Sample 1 had a tensile-strength retention rate of 85%.

<u>Sample 2</u>

Sample 2 is different from Sample 1 in that the core strand was primarily twisted. In this case, a RFL treatment solution was applied to the polyarylate fiber strand used in Sample 1. Thereafter, it was primarily twisted at a rate of 2.0 times/25 mm, which further was heat-treated. Thus, a core strand was produced. Then a cord 2A was produced by the same method as that employed for producing the cord 1A of Sample 1 except that the core strand obtained above was used.

The cord 2A thus obtained was subjected to the overcoating treatment by the same method as in the case of Sample 1. Thus, a cord 2B was obtained. The tensile strength and the elongation (%) at rupture of this cord 2B were measured. The tensile strength (initial) per cord 2B was 1200 N/cord, while the elongation at rupture was 3.0%.

Furthermore, using the cord 2B, a specimen for the bending test was produced in the same manner as in the case of Sample 1 and was subjected to the bending test. Then the tensile-strength retention rate (%) of the specimen after the bending test was determined.

<u>Comparative Sample 1</u>

First, 11 glass fiber strands produced for Sample 1 were bundled and finally twisted. Then this was subjected to the overcoating treatment by the same method as that employed for Sample 1. Thus a cord of Comparative Sample 1 was produced. With respect to this cord, the initial tensile

strength and elongation (%) at rupture were measured. Furthermore, using the cord of Comparative Sample 1, a specimen for the bending test was produced in the same manner as in the case of Sample 1 and was subjected to the bending test. Then the tensile-strength retention rate (%) of the specimen after the bending test was determined.

Comparative Sample 2

First, 2 polyarylate fiber strands used in Sample 1 were prepared. Each of them was subjected to the RFL treatment and then was primarily twisted. Next, the two strands thus obtained were bundled and finally twisted. Thus a cord was obtained and then was subjected to the overcoating treatment by the same method as that employed for Sample 1. Thus a cord of Comparative Sample 2 was produced. With respect to this cord, the initial tensile strength and elongation (%) at rupture were measured. Furthermore, using the cord of Comparative Sample 2, a specimen for the bending test was produced in the same manner as in the case of Sample 1 and was subjected to the bending test. Then the tensile-strength retention rate (%) of the specimen after the bending test was determined.

Comparative Sample 3

First, polyarylate fibers and glass fibers used in Sample 1 were mixed together without being separated into the core strand and the outer strands, which then was twisted. The number of twists was set at 2.0 times/25 mm. A cord thus obtained was subjected to the overcoating treatment by the same method as that employed for Sample 1. Thus a cord of Comparative Sample 3 was produced. With respect to this cord, the initial tensile strength and elongation (%) at rupture were measured. Furthermore, using the cord of Comparative Sample 3, a specimen for the bending test was produced in the same manner as in the case of Sample 1 and was subjected to the bending test. Then the tensile-strength retention rate (%) of the specimen after the bending test was determined.

Table 3 indicates evaluation results with respect to five types of samples thus obtained.

Table 3

	Reinforcing Fibers		Diameter of Section [mm]	Linear Density [g/1000m]	Initial Tensile Strength [N/cord]	Elongation at Rupture [%]	Tensile-Strength Retention Rate after Bending Test [%]
	Center Part	Peripheral Part					
Sample 1	Poly-arylate Fibers	9 E-Glass Strands	1.20	1580	1250	3.2	85
Sample 2	Poly-arylate Fibers	9 E-Glass Strands	1.22	1580	1200	3.0	70
Comparative Sample 1	11 E-Glass Strands	–	1.13	1440	890	3.5	51
Comparative Sample 2	2 Poly-arylate Fibers	–	1.00	860	1020	2.9	45
Comparative Sample 3	Polyarylate Fibers and E-Glass Fibers		1.28	1580	1100	3.4	65

As shown in Table 3, the cords in which only the polyarylate fibers or glass fibers were used as reinforcing fibers had lower initial strength and lower strength after the bending test. Furthermore, in Comparative Sample 3 in which glass fiber strands were not arranged to surround a polyarylate fiber strand, the initial strength, elongation at rupture, and strength after the bending test were insufficient. Particularly, in Comparative Sample 3, the elongation at rupture was high. A cord with a high elongation at rupture has a problem in that the dimensional stability thereof is lower, and when it is used for a toothed belt, the tooth part thereof tends to be damaged. Hence, it is preferable that the elongation at rupture be as low as possible. In Sample 2 in which the polyarylate fiber strand was primarily twisted, the elongation at rupture was particularly low.

On the other hand, the reinforcing cord of the present invention in which the glass fiber strands were arranged around the polyarylate fiber strand had a high initial strength, a lower elongation at rupture, and a high tensile-strength retention rate after the bending test. These values were considerably higher than those of Comparative Sample 3 in which the polyarylate fibers and the glass fibers were mixed simply together.

Industrial Applicability

The present invention is applicable to a reinforcing cord for rubber reinforcement that is suitable for reinforcing various rubber products. Furthermore, the present invention is applicable to various rubber products that are reinforced with a reinforcing cord for rubber reinforcement of the present invention. For instance, the present invention is applicable to rubber belts such as a toothed belt and a move belt, and rubber crawlers.